Regolith formation rate from U-series nuclides: Implications from the study of a spheroidal weathering profile in the Rio Icacos watershed (Puerto Rico)

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Abstract :

A 2m-thick spheroidal weathering profile, developed on a quartz-diorite in the Rio Icacos watershed (Luquillo Mountains, eastern Puerto Rico), was analysed for major and trace element concentrations, Sr and Nd isotopic ratios and U-series nuclides (^{238}U-^{234}U-^{230}Th-^{226}Ra). In this profile a 40 cm thick soil horizon is overlying a 150 cm thick saprolite which is separated from the basal corestone by a ~40 cm thick rindlet zone. The Sr and Nd isotopic variations along the whole profile imply that, in addition to geochemical fractionations associated to water-rock interactions, the geochemical budget of the profile is influenced by a significant accretion of atmospheric dusts. The mineralogical and geochemical variations along the profile also confirm that the weathering front does not progress continuously from the base to the top of the profile. The upper part of the profile is probably associated with a different weathering system (lateral weathering of upper corestones) than the lower part, which consists of the basal corestone, the associated rindlet system and the saprolite in contact with these rindlets. Consequently, the determination of weathering rates from ^{238}U-^{234}U-^{230}Th-^{226}Ra disequilibrium in a series of samples collected along a vertical depth profile can only be attempted for samples collected in the lower part of the profile. Geochemical and mineralogical data of the corestone-rindlet system that the fresh quartz diorite bedrock of the Puerto Rico system is characterized by primary mineralogical heterogeneities at the decimetric scale; such heterogeneities might complicate the application of U-series disequilibria for the determination of weathering rates. Due to the complexity of such a weathering system, only one of the two initially sampled rindlet series, along with the lower part of the saprolite, have been used for the determination of weathering rates. Similar propagation rates were derived for the rindlet system and the saprolite by using classical models involving loss and gain processes for all nuclides to interpret the variation of U-series nuclides in the rindlet-saprolite subsystem. The consistency of these weathering rates with average weathering and erosion rates derived via other methods for the whole watershed provides a new and independent argument that, in the Rio Icacos watershed, the weathering system has reached a geomorphologic steady state. Our study also indicates that even in

54 environments with differential weathering, such as observed for the Puerto Rico site, the radioactive
55 disequilibrium between the nuclides of a single radioactive series (here ^{238}U-^{234}U-^{230}Th-^{226}Ra) can
56 still be interpreted in terms of a simplified scenario of homogeneous weathering. Our work also
57 highlights the viability of coupling ^{230}Th-^{234}U and ^{226}Ra-^{230}Th disequilibrium to determine
58 weathering rates in a differential weathering context. Incidentally, the U-Th-Ra disequilibrium in
59 the corestone samples confirms that the outermost part of the corestone is already weathered.
60

1- Introduction

Quantification of regolith formation rates is important for the understanding of the formation of weathering profiles and for the prediction of their evolution in response to environmental modification due to tectonic, climatic or anthropogenic forcings (e.g., Banwart et al., 2011; Brantley,2008; Brantley et al., 2007). Analysis of U-series nuclides in soils and weathering profiles is one of only few radiochronological methods that allow direct determination of regolith production rates (e.g., Rosholt, 1982; Chabaux et al, 2003; 2008; Dosseto et al., 2008). Other chronometrical approaches, such as cosmonuclides chronometry provide information on denudation rates (e.g., Brown et al, 2003; von Blanckenburg, 2005; Braucher et al., 2009). Denudation rates derived by these methods can be compared with production rates determined by U-series nuclides in order to evaluate the balance between mean regolith production and erosion through time. In addition, the mean regolith production rates determined by U-series in weathering profiles can be compared with the present day weathering rate inferred from the analysis of river water chemistry. Such combined estimations will yield relevant information about the stability of weathering profiles (e.g., Ma et al., 2010).

In the mid-1960s, U-series nuclides became recognized as a potential tool for identifying regolith production rates (Rosholt et al., 1966; Hansen et Stout, 1968). Studies in this field of research, however, progressed only recently (Boulad et al., 1977; Mathieu et al., 1995; Dequincey et al., 1999; 2002; Chabaux et al., 2003b; Dosseto et al., 2008; 2011; Blaes et al., 2009; Pelt et al., 2008; Ma et al., 2010; 2011), mainly stimulated by the analytical improvements that have been made during the last decade for the measurement of ^{238}U-series nuclides (see Bourdon et al., 2003; Chabaux et al., 2008). The recent focus on U-series isotopes is a consequence of an increasing awareness that the determination of weathering timescales is key for understanding and modeling the evolution of the continental surfaces and their response to the near future expected environmental changes (e.g., Brantley, 2010).

86 Several recent studies have provided theoretical elements for the use of U-series nuclides in
87 weathering profiles and for the calculation of regolith weathering rates (e.g., Dequincey et al., 2002;
88 Chabaux et al., 2003b; 2008; Dosseto et al., 2008; Chabaux et al., 2011). Principally, this approach
89 requires to analyze a series of samples along the main weathering direction. Using a realistic model
90 describing the behaviour of U-series nuclides during weathering, the U-series data can be used for
91 constraining the model parameters (mobility coefficients of U-series nuclides and time since onset
92 of weathering or regolith production rates depending on the chosen model). Such studies showed
93 that the modelling approach is well suited to relatively simple alteration systems such as the
94 weathering of basaltic clasts (Pelt et al., 2008; Ma et al., 2011) or of weathering profiles developed
95 over shale(Ma et al., 2010) or andesite (Dosseto et al., 2011). On the other hand, for weathering
96 profiles with more complex history such as lateritic profiles, the data interpretation in terms of
97 propagation of weathering rates is more difficult (e.g., Dequincey et al., 2002; Chabaux et al.,
98 2003b).
99 The aim of the present study is to pursue the application of radioactive disequilibria methods to the
100 study of soil and weathering profiles in order to yield information on the regolith formation rate and
101 the regolith residence time in these profiles. We analyzed ^{238}U-^{234}U-^{230}Th-^{226}Ra nuclides in a 2m-
102 thick spheroidal weathering profile developed over a quartz diorite in the Rio Icacos watershed
103 located in a tropical rain forest of the Luquillo Mountains, eastern Puerto Rico. This site has been
104 previously extensively studied for elucidating weathering and erosion processes.
105 The Rio Icacos watershed has one of the fastest chemical weathering rates of granitoid rocks ever
106 documented for the Earth's surface (e.g., Millot et al., 2002; Viville et al., 2011; White et al., 1998).
107 For example, streamwater solute fluxes and mineral stoichiometries yield short-term chemical
108 weathering rates of 58 and 75±38 mm/kyr (Brown et al., 1995; White et al.,1998; McDowell and
109 Asbury, 1994; Turner et al., 2003). Long-term surface denudation rates have been estimated to be
110 between 43±15 and 75±18 mm/kyr using immobile element enrichments and soil ^{10}Be
111 concentrations (Riebe et al., 2003; Brown et al., 1995). Recent watershed scale Sr isotope mass

balance calculations yield a denudation rate of 68±4 mm/kyr (Pett-Ridge et al., 2009a). Therefore, these results point to a similarity between short-term and long-term weathering and denudation rates at this site, and suggest that the chemical weathering and physical erosion processes have reached steady-state in the Rio Icacos watershed (Turner et al., 2003). Consequently, a more specific goal of this study is to provide a new and independent quantification of the regolith formation rate in the Rio Icacos watershed from the U-series isotope data. The analysis of U-series nuclides is therefore associated to the analysis of major and trace element concentrations as well as Sr and Nd isotopic ratios, which are indeed relevant to constrain the principal geochemical processes co-occurring during regolith formation and causing U-Th-Ra mobilities (e.g., Dequincey et al., 2002; Pelt et al., 2008).

2-Study area and sample collection

The Rio Icacos watershed is located in a lower montane wet colorado forest (*Cyrilla racemiflora*) in the Luquillo Mountains of eastern Puerto Rico. The 326 ha basin ranges in elevation from 600 to 800 m. The mean annual temperature is 22 °C and average rainfall is 4200 mm. This watershed is 97 % underlain by the Rio Blanco stock, a quartz diorite intrusion of early Tertiary age (45 Ma) (Seiders, 1971; Cox et al., 1977), and 3 % by a quartz-free metavolcanic rock. The Rio Blanco stock is medium to coarse grained and dominated by phenocrysts of quartz and plagioclases with lesser amounts of biotite, hornblende, and chlorite; minor K-feldspar; and accessory magnetite, sphene, apatite and zircon (White et al., 1998). In the Rio Icacos basin, the regolith profile usually consists of a up to 100 cm thick bioturbated soil layer, classified as inceptisol (Buss et al.,2008) and an oxidized unbioturbated saprolite layer which can have quite variable thicknesses ranging from 100 cm to 800 cm. The saprolite consists of quartz, altered biotite (oxidized and depleted in K, Mg and Fe), kaolinite and iron oxides (goethite) (White et al., 1998). The quartz diorite bedrock is marked by spheroidal weathering, that loosens and disintegrates the bedrock, creating quartz diorite corestones separated from the saprolite by a succession of concentric layers up to 4 cm thick each,

called rindlets (Turner et al., 2003; Buss et al., 2008). Such alteration processes produce weathering profiles, which may contain residual or relict corestones of varying size depending on their vertical position in the saprolite (Fletcher et al., 2006).

For this study, a complete weathering profile developed upward from a corestone exposed at a road cut on Route 191 (details in Buss et al., 2008), was sampled in January 2006 and March 2008 (Fig.1). This profile, hereafter called "outcrop profile", is composed of a 40 cm thick soil layer overlying a 150 cm thick saprolite layer which is separated from the corestone by a ~40 cm thick rindlet zone (Fig.1). The regolith samples were collected at about 20 cm intervals; in addition, 15 rindlet samples surrounding the corestone were collected.

Due to the presence of quartz diorite corestones in the upper part of the saprolite, the vertical sampling line through saprolite had to be displaced laterally by about 20 cm at a depth of 120 cm (Fig.1). At this depth the visual characteristic of the saprolite slightly changes from a rather orange color below 120 cm to a browner one above. In the following, the saprolite is thus subdivided into a lower and upper saprolite layer, respectively (Fig.1). The rindlets just below the sampling line were previously sampled in 2003 and 2004 and analyzed by Buss et al. (2008). The rindlets collected for the present study originate from the same corestone, but offset 1m laterally from those taken before (Fig.1). These latter rindlets show mineralogical and chemical differences when compared to the underlying corestone samples. For this reason some of the rindlets sampled in 2003/2004, which are petrologically more similar to the bedrock samples have also been analyzed in the present study. The position and the nomenclature of all these samples along the profile are given in Fig1.

3-U-series methodology and analytical methods

3-1 U-series modeling

As discussed previously, the determination of regolith production rates from U-series nuclides in weathering profiles relies on the assumption that fractionation among U-series nuclides is only

controlled by weathering processes (Dequincey et al., 2002; Chabaux et al., 2003b; 2011; Dosseto et al., 2008; Ma et al., 2010; Pelt et al., 2008). These studies have also shown that the mobility of radionuclides during alteration/weathering processes can be represented by the combination of nuclide losses due to mineral dissolution and nuclide gains via illuviation or dust deposition. Given the nature of soil formation, nuclide losses and gains are usually considered as continuous processes. In the first studies, only U nuclides were assumed to be mobile whereas Th nuclides were assumed to be immobile (Chabaux et al., 2003b; Pelt et al., 2008; Ma et al., 2011). However, it has now been illustrated that Th isotopes can also be mobilized under specific weathering conditions (Dosseto et al., 2008; Ma et al., 2010; Rihs et al., 2011). Therefore, equations for Th mobility, similar to those used for U isotopes, must be incorporated to describe the system. In all these equations, the nuclide loss is represented by a first order kinetic rate law and the nuclide gains by zero order rate laws.

Herein, the regolith production rate of the Puerto Rico quartz diorite system will be derived by using such a model; however, in contrast to previous studies, the ^{226}Ra nuclide, the direct daughter of ^{230}Th, will be incorporated in the model calculations in addition to U and Th isotopes. Thus, for this study, the whole ^{238}U-^{234}U-^{230}Th-^{226}Ra disequilibria will be analysed. The evolution with time of the isotope abundance along with the evolution of the ^{232}Th abundance is then described by the following 5 equations:

$$\frac{\partial {}^{238}U}{\partial t} = f_{238}\,{}^{238}U_0 - k_{238}\,{}^{238}U - \lambda_{238}\,{}^{238}U \quad (1)$$

$$\frac{\partial {}^{234}U}{\partial t} = f_{234}\,{}^{234}U_0 - k_{234}\,{}^{234}U - \lambda_{234}\,{}^{234}U + \lambda_{238}\,{}^{238}U \quad (2)$$

$$\frac{\partial {}^{230}Th}{\partial t} = f_{230}\,{}^{230}Th_0 - k_{230}\,{}^{230}Th - \lambda_{230}\,{}^{230}Th + \lambda_{234}\,{}^{234}U \quad (3)$$

$$\frac{\partial {}^{226}Ra}{\partial t} = f_{226}\,{}^{226}Ra_0 - k_{226}\,{}^{226}Ra - \lambda_{226}\,{}^{226}Ra + \lambda_{230}\,{}^{230}Th \quad (4)$$

$$\frac{\partial {}^{232}Th}{\partial t} = f_{232}\,{}^{232}Th_0 - k_{232}\,{}^{232}Th - \lambda_{232}\,{}^{232}Th \quad (5)$$

187

188 λ_i are the decay constants (in yr^{-1}) of nuclides i (here ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra and ^{232}Th), k_i are the
189 first-order rate constants (in yr^{-1}) of nuclides i and f_i are the input fluxes (in yr^{-1}) of nuclides i
190 gained by the regolith; t is the time since the onset of weathering, i.e. when the mineral-water
191 interfacial area became large enough that fractionation of the U-series isotopes occurred.

192 Solving the above system of equations to determine the propagation rate of a weathering front
193 usually relies on the assumption that the weathering front progresses along one direction. By
194 collecting and dating a series of samples along this direction, the duration of exposure to
195 weathering of these soil samples can be estimated as a function of the distance from the weathering
196 front. In the case of isovolumetric weathering, this variation directly yields the propagation rate of
197 the weathering advance, i.e., the regolith production rate. In the case of non-isovolumetric
198 weathering, an additional volume correction is required. In the weathering systems studied up to
199 now, such a correction has rarely been applied (Dosseto et al., 2008), as it was assumed or shown
200 that the weathering within the studied systems was more or less isovolumetric. This is probably also
201 the case for the weathering processes occurring in Puerto Rico for the rindlet systems (Turner et al.,
202 2003; Buss et al., 2008) as well as for the saprolites (White et al., 1998; 2002).

203 In all of these studies, the radionuclide mobility parameters (k_i, f_i) are not known and, therefore, the
204 analysis of the radionuclides and the determination of the related radioactive disequilibria within a
205 sample are not sufficient to calculate the time since onset of weathering, or residence time of the
206 sample. The usual approach is to consider the mobility parameters to be constant over a part of the
207 profile that is large enough to constrain the radioactive disequilibria and allow the determination of
208 (1) the mobility parameters and (2) the residence time (i.e. time since onset of weathering) of the
209 samples. For example, in considering only the U-series nuclide disequilibria (^{238}U-^{234}U-^{230}Th-
210 ^{226}Ra), eight mobility parameters have to be determined to use the above differential equations. In
211 the simplest case of isovolumetric weathering, the system relies on 9 independent parameters (the
212 mobility nuclide parameters and the regolith production rate). Their determination requires the

knowledge of nine independent relationships between them if none of these parameters are known. The analysis of one sample yields 3 independent values [($^{234}U/^{238}U$), ($^{230}Th/^{234}U$) and ($^{226}Ra/^{230}Th$) activity ratios]. Analysis of at least 4 samples representing the system at different evolution stages (one reference sample and three other samples to be dated relative to the reference) is, therefore, necessary to define these 9 parameters. The use of ^{232}Th introduces two additional parameters but provides two additional values [($^{230}Th/^{232}Th$), ($^{238}U/^{232}Th$) activity ratios] for each sample. The same four samples are then characterized by 15 independent relationships, which is theoretically sufficient to determine, in addition to the 10 mobility parameters, the duration of weathering (or regolith residence time) relative to the reference sample of the other three samples. This duration represents the time elapsed since the sample was in a spatial position equivalent to the position occupied today by the "reference" sample. For such a configuration, the U-Th isotope systematics can also help to constrain the isovolumetric character of the weathering system.

In the present work, the unknown parameters, i.e. the k_i and f_i mobility parameters of each nuclide i, the average integrated regolith production rate p, or, the residence time of the different samples (if the number of independent data is large enough) is determined by a bound constrained optimization algorithm built for solving such nonlinear least-squares problems (e.g., Byrd et al., 1995; Zhu et al., 1997; Morales and Nocedal, 2011). Details are given in Appendix A. This kind of approach has been successfully implemented in the parameterization of non-linear weakly parameterized problems (di Chiara Roupert et al., 2010). Similar to other studies (Chabaux et al., 2003b; Dosseto et al., 2008; Ma et al., 2010; 2011), one has to find a range of possible parameters, which fit best the activity ratios in a way that minimizes the difference between observed and modelled values (i.e. the different activity ratios).

It is important to note that such an approach implicitly assumes that it is possible to find a zone within the weathering profile where weathering progresses along one main direction and where the different model parameters (mobility coefficients and in some cases production rates) can be considered to be constant. As shown in the following sections, the information provided by

239 mineralogical and geochemical data will help to decipher whether or not such assumptions are
240 geochemically consistent with the studied Puerto Rico profile.
241
242 **3-3 Analytical techniques**
243 The mineralogical and geochemical analyses and the isotope determinations ($^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$,
244 U-series nuclides) of the samples collected at the outcrop profile were performed at the University
245 of Strasbourg, France. Soil and saprolite samples were sieved (2 mm) and the <2mm subsamples
246 were finely powdered with an agate disk mill to ensure a complete sample digestion. The rindlets
247 sampled in 2006, hereafter named 2006 rindlets, were drilled by a 20 mm diameter diamond–steel
248 tube with diamond particles. The obtained subsamples were crushed using a hydraulic press and
249 finely powdered following the above procedure. For the remnant rindlet samples collected in 2003
250 and 2004, named 2003-2004 rindlets, all pieces were finely powdered following the above
251 procedure.
252 Major and trace element concentrations, $^{87}Sr/^{86}Sr$ isotopic ratio and U-Th-Ra disequilibria were
253 analysed for almost all outcrop profile samples, while Nd isotope ratios were determined for only a
254 few samples (see Tables 1 and 2). In addition, the mineralogical composition of one quartz-diorite
255 corestone sample, one 2006 rindlet and 3 saprolite samples were qualitatively determined by
256 powdered X-ray diffraction (XRD Brüker, D5000).
257 Major and trace element concentrations were determined by inductively-coupled plasma atomic
258 emission spectrometer (ICP-AES) and by inductively-coupled plasma mass spectrometry (ICP-
259 MS), respectively, after lithium metaborate fusion. The analytical uncertainty is < 3% for major
260 element concentrations and < 10% for trace element concentrations at 2σ (Dequincey et al., 2006).
261 For $^{87}Sr/^{86}Sr$ isotopic ratio and ^{238}U–^{234}U–^{230}Th–^{226}Ra radioactive disequilibria measurements,
262 about 200 mg of the powdered samples were spiked with a mixed ^{233}U–^{229}Th tracer and a ^{228}Ra
263 tracer (purified from Ca, Sr and Th). The Th tracers were regularly calibrated by Thermal Ionisation
264 Mass Spectrometry (TIMS) with the AThO rock standard. The sample-spike mix is then dissolved

using a three-step procedure with HNO_3–HF acids, $HClO_4$ and HCl–H_3BO_3 acids (Granet et al., 2007; 2010; Pelt et al., 2008; Ma et al., 2010).

Separation and purification of the U and Th fractions were achieved by using conventional anion exchange chromatography (Dequincey et al., 2002; Granet et al., 2007; Pelt et al., 2008). The Ra fraction was collected during the first step of the U-Th separation procedure, and then purified using a procedure adapted from the previous published separation protocols (Chabaux et Allègre, 1994; Chabaux et al., 1994; Ghaleb et al., 2004; Chmeleff, 2005). It involved three successive chromatographic separations: one for separating the Ra-Ba fraction from the main major elements and from most of REE, another one to enhance Ra-Ba purification (especially from Ca but also Sr), and a last one to separate Ra from Ba. U, Th, ^{226}Ra concentrations and U and Th isotopic ratios were analyzed in Strasbourg (LHyGeS) by TIMS on a Thermo Scientific Triton.

U concentrations and isotopic ratios were measured by using a single Re filament procedure with graphite. ($^{234}U/^{238}U$) activity ratios were calculated using the measured $^{234}U/^{235}U$ ratios and assuming a constant $^{238}U/^{235}U$ ratio of 137.88, with the decay constant in Akovali (1994) and Cheng et al. (2000).

The accuracy and reproducibility of ($^{234}U/^{238}U$) were controlled by analyzing the HU1 secular equilibrium standard solution. During the period of data acquisition (2007-2008), the mean ($^{234}U/^{238}U$) of the HU1-standard was 1.001±0.005 (n=10; 2σ). The reproducibility of U concentrations and activity ratios was checked by duplicate analyses of 4 samples and was better than 1% and 0.5%, respectively.

Th concentrations and isotopic ratios were determined using a double Re-Re filament assembly. ^{230}Th and ^{229}Th were measured on the central SEM detector and ^{232}Th on a Faraday cup using the static collection mode. During the course of this study, the of Th isotopic ratio measurements was assessed by analyzing the BRGM Th105 standard solution (Innoncent et al., 2004), $^{232}Th/^{230}Th$ = 217817± 1220 (n=7, 2σ). The reproducibility of Th concentrations and activity ratios was checked by duplicate analyses of 4 samples and was better than 1.3% and 1.1%, respectively.

291 ^{226}Ra concentrations were measured by using a single Re filament procedure with Ta_2O_5, following
292 a protocol adapted from Chabaux et al. (1994). $^{226}Ra/^{228}Ra$ ratio was measured in peak jumping
293 mode on a secondary electron multiplier associated with a pulse counting system at a temperature of
294 ~1270°C with a beam intensity between 100 and 200 cps for the minor isotope ^{228}Ra. The ^{228}Ra
295 decay of the spike was monitored by regular measurement of its $^{226}Ra/^{228}Ra$ ratio, and the ^{226}Ra
296 concentration of the spike was calibrated with AThO rock standard assuming to be at secular
297 equilibrium for ^{226}Ra-^{230}Th isotopes. The reproducibility of ^{226}Ra concentration was checked by
298 duplicate analyses of 4 samples and was better than 1.3%.
299 The Sr and Nd fractions were collected during the first stage of the chemical Ra separation. The Sr
300 fraction was purified using Eichrom's Sr Resin according to the protocol developed in the lab (Lahd
301 Geagea et al., 2007). $^{87}Sr/^{86}Sr$ ratios were measured on <600 ng Sr samples with a VG Sector mass
302 spectrometer (TIMS) using a dynamic multicollection procedure. Replicate measurements of the
303 SRM987 standard (NIST, USA) over the analysis period gave a mean $^{87}Sr/^{86}Sr$ ratio of 0.71027 ± 1
304 (n= 11; 2σ).
305 The Nd fraction was separated from the other elements using Eichrom's TRU Resin in series with
306 Eichroms Ln Resin following a procedure adapted from those already published (Pin and
307 Zalduegui,1996; Stille et al., 2009). The Nd isotopic compositions were determined on a Neptune
308 instruments MC-ICP-MS. The Merck solution yields $^{143}Nd/^{144}Nd$=0.51172±2 (2σ, n=29) and the La
309 Jolla standard analysis gave a mean $^{143}Nd/^{144}Nd$ ratio of 0.51184±1 (2σ, n=6) .
310 The total procedure blanks were < 15 pg for U, 300 pg for Th, 0.07 fg for Ra, 0.5 ng for Sr and <14
311 pg for Nd which is negligible (<1‰) compared to the amount of elements analyzed in the studied
312 samples.
313
314 **4- Results and first interpretations**
315 **4-1. Mineralogical and petrological observations through the outcrop profile**

316 Weathering of the quartz diorite has been shown to develop relatively spheroidal corestones that are
317 separated by 40- to 50-cm thick sets of rindlets of approximately 2 cm thickness each. Corestones
318 seem to form one on top of another in a vertical profile (Turner et al., 2003; Fletcher and Brantley,
319 2010). At our sampling site, we sampled the lowermost visible corestone, its rindlets, and the
320 saprolite above the rindlets. However, two corestones higher in the profile could be seen (Figure 1).
321 The profile was therefore considered to be physically structured and was subdivided into five
322 different compartments (Fig.1): the lowermost quartz diorite corestone, the rindlet zone, the lower
323 saprolite, the upper saprolite, and the soil. The upper and lower saprolite zones were delineated
324 roughly as the upper part where two visible corestones are embedded within the saprolite and the
325 lower part directly above the lowermost corestone. The corestones embedded within the upper
326 saprolite are smaller than the lowermost corestone and do not have rindlet sequences associated
327 with them, although surficial fractures indicate incipient rindlet formation. This observation
328 suggests the possibility that these corestones, along with the upper saprolite, were transported
329 during a landslide and deposited on top of the lower saprolite profile. Strictly speaking, if this were
330 the case, the upper saprolite would more appropriately be termed ‘regolith’ as ‘saprolite’ is, by
331 definition, formed in place. However, for simplicity, we will continue to use the term saprolite.
332 The lowermost quartz diorite corestone mainly consists of plagioclase, quartz, hornblende and
333 biotite, consistent with previous analyses of the Rio Blanco quartz diorite (Seiders 1971; White et
334 al., 1998; Murphy et al., 1998; Turner et al., 2003; Buss et al., 2008). In addition, traces of kaolinite
335 were detected in some of the samples. This is consistent with the observation of Fe-rich chlorite and
336 kaolinite resulting from biotite alteration in the bedrock (Murphy et al., 1998; White et al., 1998;
337 Buss et al., 2008).
338 As mentioned in the previous sections, the rindlet samples collected in 2006 have petrological and
339 mineralogical characteristics different from those of the corestone samples and the 2003-2004
340 rindlets. The 2006 rindlets contain the same minerals as the corestone but with larger quantities of
341 mafic minerals such as amphibole and the plagioclase is less abundant and finer grained than in the

342 corestone samples (Fig.2). This explains the darker colour of these rindlets compared to those of the
343 corestone and of the 2003-2004 rindlets. The texture of the 2006 rindlet zone is comparable to that
344 of magmatic xenoliths or a chilled margin zone and the texture is primary rather than the result of
345 alteration (Fig.2). Similar xenoliths are seen in quartz diorite corestones throughout the watershed
346 (in Seiders 1971; Perez, 2008). These xenoliths are more resistant to weathering than the
347 surrounding quartz diorite as evidenced by their raised appearance on rounded corestones found in
348 streams and channels. The plagioclase in the 2006 xenolith-rindlets does not appear to be more
349 altered than that in the corestone. The saprolite mineralogy is similar to that reported previously for
350 the nearby LG-1 profile (White et al., 1998): quartz, goethite, weathered biotite and kaolinite.
351 However, as described above, the saprolite sampled in the present study can be subdivided into two
352 parts. Our observations indicate that these two zones are marked by some mineralogical differences:
353 the upper part of the saprolite with two smaller corestones (Fig.1) is enriched in primary minerals
354 compared to the lower part and has a plagioclase content > 5 % (detection limit of the XRD
355 technique used) while in the lower saprolite (and at the LG1 site; White et al., 1998), the
356 plagioclase content is below detection limit .
357
358 **4-2- The evolution of the chemical composition in the different lithological units**
359 Major element concentrations of the corestone samples (Table 1) are in the range of those
360 previously determined for the quartz- dioritic bedrock of the Rio Icacos Basin (Seiders, 1971; White
361 et al., 1998; Turner et al., 2003).
362 Compared to the corresponding corestone and the 2003-2004 rindlets studied by Buss et al. (2008),
363 the 2006 rindlets are slightly enriched in Mg and Mn but depleted in Si (Fig.3); this is consistent
364 with the observed enrichment in amphibole in the rindlets studied here (see above) and, thus, is a
365 characteristic of the primary mineralogical composition. The comparison of these data in the Mafic-
366 Felsic-Weathering (MFW) ternary diagram (Fig.4), previously used to distinguish magmatic
367 differentiation trends from alteration-related trends in weathering profiles (Ohta et al., 2007),

368 confirms this suggestion. The quartz diorite data together with those already published for the same
369 pluton define a large variation trend along the FM axis, which corresponds to the magmatic
370 differentiation axis in the MFW triangle (Ohta et al., 2007). The 2006 rindlets plot at the end of this
371 trend close to the mafic corner and slightly outside the field defined by the corestones (Fig.4).
372 However, the 2003-2004 rindlets discussed by Buss et al. (2008) and collected about 1 m laterally
373 from the 2006 rindlets (Fig.1) contain less mafic compounds. They plot close to but to the right of
374 the corestones and, therefore, tend toward the weathering trend defined by the saprolite samples in
375 the MFW triangle.
376 Above the rindlet-saprolite contact (at 210 cm depth) the MgO, CaO, Na_2O, K_2O concentrations
377 strongly decrease, whereas TiO_2, Fe_2O_3 and Al_2O_3 concentrations increase, relative to the samples
378 below (Fig.5 and Table 1). Such variations, as previously observed in Puerto Rico profiles, can be
379 linked to weathering processes, as attested by the position of the saprolite data point in the MFW
380 diagram (Fig.4). However, within the saprolite, above the interface between lower and upper
381 saprolite (at ≈120 cm depth), the Al_2O_3 concentrations significantly decrease from about 22 to <15
382 wt. %; also MgO decreases again to lower concentrations. Similarly TiO_2 contents decrease from
383 0.7 % o < 0.6 wt. % and Fe_2O_3 contents decrease from 12 to <9 wt. %. The abrupt shift in
384 composition between the upper and lower saprolite is also consistent with the hypothesis that the
385 upper saprolite could represent a landslide deposit.
386 The Rare Earth Element (REE) concentrations of the saprolite samples normalized to the corestone
387 also confirm significant differences between lower and upper saprolite zones (Fig. 6). Saprolites
388 close to the rindlet contact (06PR02,03,32) are less depleted in REE relative to the corestone,
389 compared to higher saprolite samples.. Samples 06PR02 and 03 also show negative Eu anomalies
390 and significant positive Ce anomalies (Ce/Ce*= 2). With decreasing depth, all REE concentrations
391 decrease below those of the corestone. In contrast, the REE concentrations of the upper saprolite are
392 always lower than those of the corestone and the Eu and Ce anomalies have nearly disappeared.

393 Zr and Hf concentrations change significantly within the outcrop profile. In particular, the 2006
394 rindlets are marked by much lower Zr (20 ppm-30 ppm) and Hf (around 1 ppm) concentrations than
395 the quartz diorite (100-193 ppm) and the 2003-2004 rindlets (80-150 ppm) (Fig.7). Similar
396 differences exist between lower and upper saprolite. Nevertheless, the Zr/Hf ratios in the saprolite is
397 relatively constant (~ 40) and similar to that in the corestone; whereas the 2006 rindlets show much
398 lower Zr/Hf ratios ranging between 18 and 25 (Fig.7). The occurrence of such low Zr/Hf ratios
399 might be related to specific magmatic processes involving crystallization of amphibole and
400 pyroxene (not observed), which preferentially incorporate Hf over Zr (Linen and Keppler, 2002).
401 Such a process might have occurred in the protolith of the 2006 rindlets which have structures
402 reminiscent of a chilled margin and are enriched in amphibole and are visually similar to mafic
403 xenoliths observed in corestones throughout the watershed. Thus, the Zr depletion in the 2006
404 rindlets and the associated low Zr/Hf ratios are rather the result of magmatic processes involving
405 fractional crystallization of amphibole rather than due to weathering process. The fact that the
406 saprolite carries Zr/Hf ratios similar to those of the corestone and not to the 2006 rindlets indicates
407 that the corestones, rather than the xenoliths, represent the protolith for most of the saprolite. In
408 addition, the fact that the 2003-2004 rindlets are free of fine-grained mafic compounds (Buss et al.,
409 2008) and have corestone-like Zr/Hf ratios supports this idea and suggests that the chilled margin-
410 like structure is rather a very small-scale local phenomenon. Indeed, such xenoliths, while not
411 uncommon in the Rio Blanco quartz diorite (e.g., Seiders, 1971; Perez, 2008), are also not abundant
412 and tend to be small (typically < 15 cm diameter). Because of these very special characteristics of
413 the 2006 rindlets, they will be not used for U-series dating. More details on these rindlets, including
414 U-series nuclide composition are given in electronic Appendix EA1.
415
416 **4-3. The evolution of the Sr and Nd isotopic compositions in the different lithological units**
417 The Sr isotopic compositions of the corestone are low and range between 0.70397 and 0.70440.
418 These values are similar to quartz diorite values reported by Pett-Ridge et al. (2009a) and Jones and

419 Kesler (1980). They are also similar to the $^{87}Sr/^{86}Sr$ ratio (0.70411) reported for the adjacent
420 volcanoclastic rocks (Frost et al., 1998). The slightly higher isotopic ratios of some corestone
421 samples (up to 0.7044) might be indication of beginning, but still weak, alteration. The rindlet Sr
422 isotopic compositions vary between 0.70390 and 0.70397. Their similarity to the corestone isotopic
423 compositions points again to their close magmatic relationship. At the interface between rindlet and
424 lower saprolite (at 205 cm depth) the $^{87}Sr/^{86}Sr$ ratios increase to 0.71227 and then decrease at 120
425 cm depth at the transition zone between lower and upper saprolite (Fig. 8a). In the upper saprolite a
426 further decrease of the Sr isotopic composition with decreasing depth is observed and continues into
427 the overlying 20 cm thick soil (Fig.8a). The trends in Sr isotopes in the two saprolite zones is
428 consistent with the landslide hypothesis. The high $^{87}Sr/^{86}Sr$ ratio at the top of the lower saprolite
429 (0.71227) is in between ratios reported by Pett-Ridge et al. (2009) for the surface soil from the
430 undisturbed LG-1 ridge top (0.71080) and for local atmospheric input (0.71343). The trend in
431 $^{87}Sr/^{86}Sr$ between this high value at the upper-lower saprolite interface and the low value of the
432 corestone describes a mixing line similar to that observed by Pett-Ridge et al. (2009). Subsequent
433 burial of the lower saprolite by a landslide bearing less-weathered saprolite would result in an upper
434 saprolite zone that has a lower $^{87}Sr/^{86}Sr$ ratio, as observed.
435 The ε_{Nd} value of the corestone is +6.7 which is very close to the previously published bedrock ε_{Nd}
436 value of +7 (Pett-Ridge et al., 2009a). As for Sr isotopic ratios, the Nd isotopic compositions of the
437 rindlets are similar to those of the corestone and, therefore, confirm the same magmatic source for
438 all of these samples. The ε_{Nd} values of the saprolite samples decrease with decreasing depth from
439 +5.2 at 200cm depth to ≈ 0 at 80cm depth. Then the ε_{Nd} increases again and reaches an ε_{Nd} value of
440 +5 close to the surface (Fig.8a).
441
442 **4-4. The U-Th-Ra disequilibria**

443 The ($^{234}U/^{238}U$) ratios slightly increase from the corestone to the top of the saprolite (Fig. 8).
444 However, U-Th concentrations and ^{238}U-^{234}U-^{230}Th-^{226}Ra isotopes do not show simple trends along
445 the weathering profile from the corestone to the top of the soil. The trends are detailed below.
446
447 -*Corestone:*
448 The systematic occurrence of radioactive disequilibria among the U-series nuclides within the five
449 corestone samples indicates that all of them have already been weathered to some extent. Indeed, an
450 unweathered bedrock older than 1 Myr must be in secular equilibrium (i.e. ($^{234}U/^{238}U$) =
451 ($^{230}Th/^{238}U$) = ($^{226}Ra/^{230}Th$) = 1). Here, the values of ($^{234}U/^{238}U$) and ($^{230}Th/^{238}U$) (Fig. 8) for the
452 corestone samples are all significantly > 1. This observation is consistent with the presence of traces
453 of kaolinite in some of the corestone samples. It is also consistent with the fact that all corestone
454 samples analysed for this study are located at the periphery of the corestone (Fig. 1) which has been
455 shown to be affected by incipient weathering including biotite oxidation (Buss et al., 2008). The
456 ($^{230}Th/^{238}U$) activity ratios of the corestone samples are all >1 (1.21 to 1.30) and suggest that this
457 incipient weathering is marked either by U leaching or Th gain (Fig. 8). However, all corestone
458 samples are also characterized by ($^{234}U/^{238}U$) >1, which cannot be explained by simple U loss (Fig.
459 8). If Th is assumed to be immobile during incipient weathering, then it is possible that ^{234}U uptake
460 occurs concurrently to ^{238}U loss. Therefore, even during the early stages of weathering, the mobility
461 of the different radioactive nuclides must be described in term of enrichment and depletion. The
462 position of the samples around the corestone does not allow to use these data for calculating the
463 propagation rate of this incipient weathering front within the corestone: a radial transect across the
464 corestone would be required.
465
466 -*Rindlets* and saprolite
467 Compared to the corestone samples, most of the remnant 2003-2004 rindlets have very similar Th
468 concentrations but higher U concentrations (~0.4ppm) (Table 2). This might point to U enrichment

during rindlet formation without significant Th mobility. The observation of a ($^{234}U/^{238}U$) activity ratio >1 in these rindlets is consistent with this hypothesis. From the corestone to the outer rindlets, the ($^{230}Th/^{232}Th$) activity ratio increases and the ($^{230}Th/^{238}U$) activity ratio decreases while ($^{226}Ra/^{230}Th$) activity ratios are constant but slightly >1 (Fig. 8b,c). As observed above, the variations of U and Th concentrations or U-series disequilibria are very different between the upper and lower saprolites. This is well illustrated by the U/Th, the ($^{230}Th/^{232}Th$) or ($^{234}U/^{238}U$) (Fig. 8) ratios which are smaller in the lower saprolite than in the upper saprolite.

5-Discussion

5-1 Variations of the major and trace element concentrations in bedrock and rindlets.

The similarity between the REE patterns of the corestone samples and the rindlet samples (not shown) along with their close Sr-Nd isotopic ratios point to the common magmatic origin of all of these samples. The petrological and geochemical data suggest, however, as already noticed in previous studies on the Rio Blanco stock (Turner et al., 2003; Buss et al., 2008), that the corestone-rindlet system is not mineralogically homogeneous at the centimetre or decimetre scale. Thus, for the discussion of the mobility of chemical elements during the weathering of the quartz diorite bedrock and the formation of rindlets and saprolite, an average chemical composition of the fresh bedrock has been used as reference. This allows identification of the mineralogical sequence of quartz diorite weathering within the rindlet zones (Turner et al., 2003; Buss et al., 2008). The bedrock was first affected by biotite oxidation which began in the corestone and results in a loss of K across the rindlet zone; it is followed by plagioclase weathering across the rindlet zone causing Na and Ca loss; finally hornblende weathers, first by oxidation and then by rapid and complete weathering within the outermost rindlets to form material that was termed “protosaprolite” in an earlier publication (Buss et al., 2008). The six 2004 rindlets analyzed here belong to this trend of weathering. They constitute a relatively simple weathering system, which is progressively modified from the base to the top of the rindlet zone by increasing biotite oxidation and plagioclase

transformation: such a weathering system is *a priori* well suited for determining the propagation rate of the weathering front with help of U-series systematics.

5-2- Variations of the major and trace element concentrations in the saprolite

As already proposed for major and trace element variations in the LG-1 profile (White et al., 1998), and confirmed by the mineralogical data obtained in this study and by Buss et al. (2008), the significant loss of mobile elements in the "outcrop" profile at the corestone/saprolite transition is mainly due to the weathering of primary minerals including plagioclase, biotite and hornblende and precipitation of secondary minerals, primarily kaolinite and goethite. Such mineralogical transformations may explain the REE distribution patterns of the lower saprolite at the contact with the rindlets. REE distribution patterns are indeed still similar to those of the rindlets but with significant positive Ce anomalies. This is consistent with precipitation of insoluble CeO_2 due to oxidation of Ce^{3+} to Ce^{4+}. This is accompanied by accumulations of oxides/hydroxides of Al and Fe probably due to dissolution of biotite as indicated by the comparatively high Fe_2O_3 and Al_2O_3 contents in the lower saprolite (Fig.5; Table 1).

As noticed in the Results section, the upper saprolite layer (between 40-120 cm depth) is more enriched in primary minerals than the basal saprolite (between 120-205 cm depth), with plagioclase and hornblende contents >5 % in the upper saprolite and not detectable in the lower one. This might point to a lesser degree of weathering in the upper saprolite than in the lower one. Such a conclusion is entirely consistent with the depth variation along the profile of loss on ignition (LOI) and of the chemical weathering index (CWI= $[(Al_2O_3+Fe_2O+TiO_2+LOI)$/sum of major oxides]*100) (Sueko, 1988), both of which can be considered as proxies for the degree of weathering. LOI is indeed lower in the upper part than in the lower part of the saprolite (Fig. 5). The CWI, which ranges classically between 13 and 15 % in unweathered granitic bedrocks and increases with weathering intensity (Taylor and Eggleton, 2001), is lower in the upper than in the lower saprolite (Fig. 5). These observations indicate that the upper part of the saprolite is less

521 weathered than the lower one. If the upper saprolite is indeed landslide debris, it was either
522 transported from a less weathered zone and/or included broken rindlets that have since disappeared.
523 An alternative, *in-situ* explanation arises from the characteristics of the spheroidal weathering
524 system, where weathering proceeds along preferential surfaces of water circulation in the rock,
525 inherited from the 3D network of prexisting bedrock joint planes. This progressively isolates
526 residual corestones in the saprolite. Therefore, depending upon the original size of a corestone
527 block, the extent of weathering at any given depth can differ significantly. Consequently, in the case
528 of spheroidal weathering, the weathering front may not progress continuously from the base to the
529 top of the profile: weathering also advances inward radially into residual corestones. For these
530 reasons, only the samples from the lower saprolite, close to rindlets and corestone and, therefore,
531 close to the weathering front, shall be used for the determination of the weathering rates by U-Th-
532 Ra disequilibria measured in a series of samples collected along a vertical depth profile.
533
534 **5-3 Variations of Sr and Nd isotopes ratios in saprolite**
535 Sr and Nd isotope data and mass balance considerations for the neighbouring LG-1 soil/saprolite
536 profile are consistent with significant deposition of atmospheric dust at that site (Pett-Ridge et al.,
537 2009a,b). This is also in agreement with McDowell et al. (1990) who noted a Saharan dust
538 component in precipitation in the Luquillo Experimental Forest. Similarly, the Sr-Nd budget in the
539 saprolite is consistent with weathering of primary minerals affected by atmospheric dust deposition.
540 For example, this is emphasized by the scatter in the ε_{Nd}-$^{87}Sr/^{86}Sr$ diagram (Fig.9) below the ε_{Nd}
541 values of primary bedrock minerals. A similar observation has been made for the Sr-Nd isotope
542 data in granite-derived soils in the Vosges mountains (France; Aubert et al., 2001; Stille et al.,
543 2006). The saprolite Sr and Nd isotope data can only be explained by an additional external
544 atmospheric source with a low continental crust-like εNd value such as Saharan dust (Pett-Ridge et
545 al., 2009a; b). Specifically, the position of the saprolite data points to the right of the theoretical
546 mixing hyperbolae between the fresh quartz diorite end-member and the atmospheric dust end-

547 member (Fig.9), is entirely consistent with deposition of atmospheric dust to soil and saprolite. The
548 observation that the samples from the lower and upper saprolite plot along two different trends in
549 the ε_{Nd}-$^{87}Sr/^{86}Sr$ diagram reinforces the interpretation of the occurrence of two different units
550 within the saprolite. The two mixing trends also support the suggestion that the upper unit is less
551 weathered than the lower one; indeed, the lower unit trend, in the ε_{Nd}-$^{87}Sr/^{86}Sr$ diagram, can be
552 explained by a larger loss of mobile elements and/or lower amount of non-radiogenic minerals, such
553 as hornblende and plagioclase. Based on the position of the data points in Fig.9, one might also
554 suggest that the outcrop profile is less affected by atmospheric deposition than the LG-1 profile
555 studied by Pett-Ridge et al. (2009a). The fact that the nature and/or intensity of atmospheric
556 deposits depends on relief and altitude of the site (e.g., Doucet and Carrignan, 2001; Pourcelot et al;
557 2003) might explain why one observes at the location of the LG1 site on a ridge top at 680 m
558 elevation more atmospheric dust than in the outcrop profile at lower elevation (<600 m).
559 Alternatively, if the upper saprolite is composed of landslide debris, it likely has been exposed to
560 atmospheric inputs for less time than saprolite/soil units formed in place in the watershed.
561 It is, however, difficult to precisely estimate the dust contribution from the mixing curve in
562 the ε_{Nd}-$^{87}Sr/^{86}Sr$ diagram since the dust particles did not mix with material of the fresh quartz
563 diorite but with Sr-depleted soil and saprolite. In addition, the saprolite-dust system underwent
564 further weathering which has offset the isotopic compositions from a pure mixing case (Pett-Ridge
565 et al., 2009a). The important point to note here is that the ε_{Nd} and $^{87}Sr/^{86}Sr$ data confirm that dust
566 accretion is an important parameter that needs to be taken into account in order to establish a correct
567 weathering mass balance calculation at the scale of a watershed as well as at the scale of a
568 weathering profile; similar assumptions have been made for Hawaiian soils (Pett-Ridge et al., 2007)
569 and soils at the Cameroun Mount (Dia et al., 2006 ; Pelt et al., 2011).
570 Dust deposition probably also influences the U and Th budget of the studied profile. However, its
571 contribution is difficult to estimate because U and Th concentrations of the aeolian dusts have to be

572 known. To the best of our knowledge, no direct measurements are available for the Puerto Rico site.
573 Nevertheless, the wind-borne Saharan dust collected at Barbados (Rydell and Prospero, 1972)
574 indicates that U and Th concentrations in aeolian particles can be high, with U and Th
575 concentrations of 3.6 and 12.4 ppm, respectively. Such concentrations are consistent with upper
576 continental crust values (2.8 and 10.7 ppm, respectively, Taylor and McLennan, 1995). These
577 concentrations are high compared to the U and Th concentrations in the upper and lower saprolite
578 (U : 0.6- 0.9 ppm ; Th : 1.2 – 2.4 ppm); Such values would imply that a deposition of about 5% of
579 atmospheric dust would for instance control about 10-15 % of U and Th in the weathering profile.
580 This rough estimation indicates that, in contrast to the comparatively weak U and Th contribution in
581 rainwater (Riotte and Chabaux,1999; Chabaux et al., 2003), U and Th dust contribution is not
582 negligible. For the Puerto Rico case, the aeolian contribution probably explains the ($^{234}U/^{238}U$)
583 ratios >1 along the weathering profile with highest values in the upper part of the saprolite, since
584 wind-borne Saharan dust is marked by ^{234}U enrichments with a ($^{234}U/^{238}U$) of up to 1.08 (Rydell
585 and Prospero, 1972). Nonetheless, dispersion of the data points in the ($^{234}U/^{238}U$) vs $^{87}Sr/^{86}Sr$ or
586 ($^{230}Th/^{232}Th$) vs ε_{Nd} diagrams (not shown) clearly suggests that the U-Th budget of the saprolite is
587 not only controlled by dust accretion but also by geochemical fractionations associated with water-
588 rock interaction in the weathering profile.
589
590 **5-4 Variations of U-series nuclides and determination of weathering rates**
591 The mineralogical and geochemical data indicate that the weathering profile is marked by a double
592 complexity, which may render the use of U-series disequilibria for the determination of the
593 weathering rates difficult. The first difficulty is that the studied profile is a spheroidal weathering
594 system that cannot be characterized by only one weathering direction. Therefore, the approach
595 proposed in §2-2 for determining weathering rates from a series of samples collected along a
596 vertical depth profile can be applied only to the samples collected within the rindlet zone and within
597 the lower saprolite. A second difficulty results from an implicit hypothesis of the model, which has

598 rarely been discussed in previous studies (Chabaux et al., 2003b; 2011). The modelling approach
599 assumes that the different samples collected along a weathering profile result from homogeneous
600 weathering of a single initial material. This is for instance the case for a Costa Rican basaltic clast
601 (Pelt et al., 2008) or the soils in the Susquehanna/Shale Hills watershed (Ma et al., 2010). In the
602 case of the Puerto Rico weathering system it appears that the corestone might have, at least locally,
603 mineralogical characteristics which are quite different from those of the mean bedrock. Such
604 mineralogical variations will influence the U-series nuclide systematics within the profile, if, for
605 instance, it induces local modifications of the nature or the intensity of the weathering processes,
606 that affect the mobility parameters of the U-series nuclides during the bedrock weathering. In this
607 case the variation of U-series nuclides along a depth profile cannot be interpreted by using the
608 modelling approach (see §2-2) because the constancy of the mobility parameters along the whole
609 depth profile is not given. A similar situation could result from differential weathering of bedrock
610 minerals, which classically lead to a change in the proportion of the primary minerals during
611 progression of the weathering reactions. If the fractionation of the different U-series nuclides varies
612 with the nature of the mineral phases, then the apparent mobility of these nuclides during the
613 weathering progress of the whole rock can no longer be considered as constant. Therefore, the
614 different equations have to involve mobility terms for each mineral and not a global one for the
615 whole rock. The number of unknown parameters would then increase considerably and, if the
616 number of samples is limited, the resolution of the equation system becomes impossible. Such
617 limitations have to be kept in mind when the U-series radioactive disequilibria are interpreted for a
618 weathering profile, especially when the nuclide ^{232}Th and hence the ($^{238}U/^{232}Th$) and ($^{230}Th/^{232}Th$)
619 activity ratios are involved (see below).
620
621 ***-Determination of production rate in the lower saprolite***
622 The complete transformation from rindlet to saprolite is reached in sample 06PR02. The sample just
623 below has intermediate geochemical characteristics between bedrock and saprock. For the

624 calculation of the weathering rate, it is therefore appropriate to use samples 06PR02 to 06PR06.
625 Sample 06PR04 has not been used as it is marked by atypical geochemical characteristics including
626 a lower degree of weathering (lower LOI and CWI) and lower Th and REE concentrations than
627 observed for the 4 other lower saprolite samples. The origin of these characteristics is not fully
628 understood but is possibly due to mineralogical heterogeneities in the parent bedrock. For the four
629 remaining lower saprolite samples, several solving configurations can be envisaged (see §2-2). The
630 first one is to consider the variation of the ^{238}U-^{234}U-^{230}Th-^{226}Ra disequilibrium across the lower
631 saprolite. This allows determination of an average weathering rate if one assumes that the
632 weathering is isovolumetric with a constant propagation rate over the time. The second
633 configuration introduces the ^{232}Th in addition to the four other nuclides. This should theoretically
634 allow for calculating the mean age of each sample and as well as the mean average production rate
635 as in the first configuration. The data of the 4 lower saprolite samples were, therefore, modelled in
636 three different ways: one by using only ^{238}U-^{234}U-^{230}Th-^{226}Ra nuclides and assuming a constant
637 regolith production rate P; the two other ones by using ^{232}Th, once by assuming P to be still
638 constant over the lower saprolite profile and once by calculating the age of each sample. Therefore,
639 in the latter approach the constancy of the regolith production rate P is not a necessary assumption.
640 The results of the three simulations are given in Table 3. They also indicate that the simulation
641 using only ^{238}U-^{234}U-^{230}Th-^{226}Ra data without ^{232}Th are a better fit to the data than the two
642 simulations using ^{232}Th. Furthermore, the mean weathering rates are different depending on
643 whether ^{232}Th is used or not. Without fitting the ^{232}Th data, the average propagation rate is
644 relatively low (≈ 45±12mm/Ma). However, the simulation results can statistically be subdivided
645 into two populations: the largest number of simulations is consistent with 45±2 m/Ma while fewer
646 simulations yield 10 ± 2 m/Ma (Fig. 10). These two populations strongly depend on the values of
647 U-Th-Ra mobility parameters used for calculation. In the first case, the leaching parameters of the
648 U-Th-Ra nuclides have relatively similar values. On the other hand, for low regolith propagation
649 rates, the Ra leaching coefficient has to be significantly higher than that of U or Th. ^{226}Ra, ^{230}Th and

650 ^{234}U nuclides derive from ^{238}U by radioactive decay and, therefore, they may occupy the same
651 crystallographic sites in minerals and their rates of liberation by leaching and/or dissolution of
652 minerals should be similar. Under these conditions a weathering rate of 45±2m/Ma can be derived
653 for the formation of the lower saprolite.
654 As also observed recently for the Shale Hill watershed (Ma et al., 2010), the use of ^{232}Th and hence
655 of ($^{238}U/^{232}Th$) and ($^{230}Th/^{232}Th$) ratios in addition to ^{238}U-^{234}U-^{230}Th-^{226}Ra nuclides yields fits to
656 data that are less close than simulations with ^{238}U-^{234}U-^{230}Th-^{226}Ra only. This might be linked to the
657 fact that ^{232}Th can occupy other crystallographic sites than ^{238}U and its decay nuclides. If two
658 nuclides are located in different crystallographic sites or even in different minerals, then release to
659 solutions could occur at different times during weathering. The quartz diorite contains minerals
660 with different ($^{238}U/^{232}Th$) and ($^{230}Th/^{232}Th$) ratios; therefore, in a context of differential weathering,
661 as observed for the Puerto Rico quartz diorite (White et al., 1998; Buss et al., 2008), weathering of
662 minerals with different ($^{238}U/^{232}Th$) and ($^{230}Th/^{232}Th$) ratios might induce "apparent fractionations"
663 of the ^{230}Th-^{232}Th and partly of the ^{238}U-^{232}Th nuclides at the whole rock scale. Such fractionations
664 might result from a change in the relative proportion of weathered mineral phases with different
665 ($^{230}Th/^{232}Th$) ratios during weathering progression. Thus, the use of ^{232}Th necessitates the additional
666 introduction of the specific mobility parameters of these different mineral phases into the model
667 equations. Given the number of parameters to be estimated, this renders the modelling more or less
668 impossible by the approach proposed in §2-2. Otherwise, the fact that the variations of the ^{238}U-
669 ^{234}U-^{230}Th-^{226}Ra data conform to a homogeneous weathering model despite differential weathering
670 is probably an indication that the relative weathering mobility of these nuclides is not very different
671 among the mineral phases.
672
673 ***-Determination of production rate in the 2004 rindlets***
674 For reasons given in part 3-3, only the 2004 rindlets are used to estimate the weathering rate. More
675 precisely, the five lower 2004 rindlets have been used because they belong to a relatively simple

676 weathering system characterized by the progressive weathering of biotite and plagioclase. The
677 outermost sample has been excluded because it has weathered to saprock, also called
678 'protosaprolite' (Buss et al., 2008), which is marked by other mineral transformations. For the five
679 remaining 2004 rindlets, the rate has been determined according to the modelling approaches used
680 for the lower saprolite. Results are given in Table 3. Assuming a constant regolith propagation rate
681 P, either with or without ^{232}Th, one calculates similar mean weathering rates but different mobility
682 coefficients for Th and Ra. The third approach seeking to determine the age of each sample did not
683 yield satisfactory results. With ^{232}Th, the simulation does not fit the data as well as the simulation
684 without ^{232}Th. The regolith production rates and mobility parameters (leaching parameters) were
685 totally different from those obtained by the two other approaches. Such differences might indicate
686 that the regolith production rate at the scale of the rindlet system is not constant over time; it could
687 also indicate, as for the saprolite, that the model is again not suitable when using ^{232}Th. Biotite can
688 be marked by (^{238}U/^{232}Th) elemental ratios and hence (^{230}Th/^{232}Th) activity ratios that are markedly
689 different from those of the whole rock (Aubert et al., 2001). Therefore, biotite weathering might
690 induce a variation of the (^{230}Th/^{232}Th) ratios in the residual rock, which is not only the consequence
691 of the chemical fractionation between uranium and thorium and time, but also of the proportion of
692 the minerals involved in the weathering process. In this case, inclusion of the ^{232}Th data in the
693 simulation may yield results that are not reliable.
694 Thus, similar to the saprolite, the determination of weathering rates will be only made by using U-
695 series nuclides. The simulation yields weathering rates quite similar to those obtained for the
696 saprolite: a population of simulations that yield weathering advance rates between 52 ± 13 m/Ma,
697 and another one between 8 ±5 m/Ma (Fig 10). The two populations only depend on the relative Ra,
698 Th and U leaching coefficients. As for the lower saprolite, the fact that the ^{234}U-^{230}Th-^{226}Ra
699 nuclides belong to the same ^{238}U series *a priori* implies that the degree of mobilization of these
700 elements during weathering is similar, which, in turn, allows for the derivation of a mean
701 weathering rate of 52 ± 13 m/Ma.

-Implications for the regolith formation.

The results obtained from the above simulations yield consistent values for the weathering advance rates of the rindlets and saprolite. The U input parameters derived from the models are also consistent with each other. For example, the U input parameters are smaller in the rindlets than in the lower saprolite in accordance with the occurrence of smaller ^{234}U enrichments in the rindlets than in the saprolite. These observations lend confidence to the reliability of the modelling results. This validates the above assumption that even in relatively complex environments with differential weathering, such as the Puerto Rico site, the radioactive disequilibrium between the nuclides of the ^{238}U-series can still be interpreted in a theoretical frame of a homogeneous weathering scenario. This, in turn implies, as noted above, that the fractionation among the nuclides of a same radioactive series during the degradation of primary minerals of the corestone is not very different from one mineral to another.

Another important result of the study is the observation of very similar propagation rates of the weathering fronts in the rindlet zone and in the saprolite. This certainly indicates that the weathering profile has reached a steady-state of functioning for the time period covered by the sampling zone (≈20 to 30 ka). This is confirmed by the observation that in the ($^{230}Th/^{234}U$) *vs.* ($^{226}Ra/^{230}Th$) disequilibria diagram, the data points of the most external samples, used for the rate determinations in the rindlet zone and the lower saprolite, plot close to the position of the theoretical steady state values obtained by assuming time variation in equations 1-5 to be equal to zero.

It is also interesting to note that the weathering rates inferred from the U-series analysis of a 2-3 m depth profile is similar to the average rate estimated for the whole watershed. This conclusion indicates that, in contrast to the Shale Hills watershed for example (Ma et al., 2010), the rate of weathering is everywhere the same regardless of the position on a hillslope or in the watershed. Although this observation has to be confirmed by studies of other weathering profiles in the Rio

728 Icacos watershed, it suggests that the weathering system reached a geomorphologic steady state
729 under such tropical climate.
730
731 **6- Conclusions**
732 The geochemical and isotopic (Sr, Nd, U-series nuclides) data of a 2-m thick spheroidal weathering
733 profile indicate that in this profile, the weathering front does not progress continuously from the
734 base to the top of the profile. This is probably due to an upper unit comprised of landslide debris,
735 although it may also be due to the spheroidal nature of the bedrock weathering system: the
736 weathering proceeds in this case along preferential surfaces of water circulation in the rock,
737 inherited from the 3D network of prexisting bedrock joint planes. The consequence is that the
738 determination of weathering rates by ^{238}U-^{234}U-^{230}Th-^{226}Ra disequilibrium is only possible in the
739 lower part of the profile, which is composed of the corestone, the related rindlet system and the
740 saprolite in contact with these rindlets. The mineralogical and geochemical data of the corestone -
741 rindlet system also indicate that the quartz diorite bedrock of the Puerto Rico system is marked by
742 important primary mineralogical heterogeneities (primarily xenoliths) at the decimetric scale, which
743 can complicate the determination of weathering rates from U-series disequilibria.
744 Intrepretation of the variation of U-series nuclides in the rindlet-saprolite system by using classical
745 loss and gain models for describing the mobility of radionuclides during weathering, allows
746 estimation of similar propagation rates of the weathering front (≈45m/Ma) in rindlets and saprolite.
747 The consistency of the derived weathering rate with the average weathering and erosion rates
748 determined by other methods for the whole watershed argues again, that in the Rio Icacos
749 watershed, the weathering system has reached a geomorphic steady state. Our results further
750 indicate that even in environments with differential weathering, such as observed for the Puerto
751 Rico site, the radioactive disequilibrium between the nuclides of a single radioactive series (here
752 ^{238}U-series) can still be interpreted in terms of a homogeneous weathering scenario. They also
753 illustrate the utility of combining the analysis of ^{226}Ra-^{230}Th disequilibria with the analysis of ^{238}U-

754 ^{234}U-^{230}Th disequilibria to constrain the weathering rates in such context. This work should
755 stimulate future development of ^{238}U-^{234}U-^{230}Th-^{226}Ra nuclides for use in constraining weathering
756 rates in weathering profiles with variable geological or environmental parameters.

757

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Table captions

Table 1 : Chemical composition of the samples. Major elements are given in oxide mass percentage and trace elements in ppm.

Table 2: U , Th, ^{226}Ra concentrations, U/Th elemental ratios, U and Th activity ratios, ($^{230}Th/^{234}U$), ($^{226}Ra/^{230}Th$) ratios, Sr isotopes ratios, εNd values.

Table 3 : Weathering propagation rate, and mobility parameters (k_i, f_i) derived for the models for the lower saprolite (a) and the 2004 rindlets (b). The model is solved multiple times to obtain about 1000 sets of solutions for each simulation, as described in Appenix A. The (P, k_i, f_i) parameters are taken as the average of the sets of solution values, and the uncertainties are calculated as the standard deviation on the sets of values.

Figure captions:

Figure 1: a-Location map of the Rio Icacos watershed (star indicates the weathering profile location in the watershed); b-sample position along the weathering profile with the name and depth of the different samples. "2003-2004" and "2006" refer to the different sets of rindlets sampled (see text for details)

Figure 2: Photographs of a cut section of a 2006 rindlet (a) and of a related thin section (b). This rindlet contains the two types of rocks encountered in the corestone-rindlet zone. The black line delimits a whiter zone (06PR28) having the same mineralogical characteristics as the quartz diorite corestone and a grayer zone, with petrological and mineralogical characteristics similar to those of the 2006 rindlets (06PR29).

Figure 3: depth variation of major element concentrations within the rindlet zone. The solid-state element concentration (C_w) is used for comparison with the rindlet data published in Buss et al. (2008). The Cw allows to take into account for the physical changes in the regolith (i.e. density, loss of elements…), by normalizing to an immobile element [$C_w = C\ (I_o/I_w)$, with C the measured concentration, I_0 the concentration of the immobile element (here Ti) in the bedrock (mol/kg) and I_w the concentration of the immobile element in the weathered sample].

Figure 4: Outcrop profile samples and previously published Rio Blanco quartz diorite corestone data in a Mafic-Felsic-Weathering (MFW) diagram (Rio Blanco quartz diorite corestone data from Buss et al., 2008 ; Riebe et al., 2003 ; Seiders, 1971 ; Turner et al., 2003 and White et al., 1998). The MFW ternary diagram, defined by Ohta et al. (2007), is elaborated from the principal component analysis (PCA) of a large dataset derived from unweathered igneous rocks (more than 110 rocks) and their weathering profiles (179 weathered samples) (details in Ohta et al., 2007). The M, F and W vertices characterize mafic (M), felsic (F) rock source and the degree of weathering (W) of these sources, respectively. W is independent of the geochemical variability of the unweathered parent rock. The variables used in the principal component analysis (PCA) were SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O and K_2O (in wt.%, see Ohta et al., 2007 for the vertice calculation). Rather than the dissolution process of a single mineral, the MFW ternary diagram predicts the weathering trends of igneous rocks, generating a picture of the bulk geochemical response to the weathering process, regardless of parent rock types.

Figure 5: Depth variation of the major element concentration along the weathering profile (major element concentrations are given in weight percent of oxides; LOI for Loss-on-ignition (in wt. %); CWI: chemical weathering index defined by CWI% = [(Al_2O_3+Fe_2O+TiO_2+LOI%)/sum of major oxides%]*100) (Sueko, 1988).

Figure 6: Rare Earth Element (REE) patterns normalized to the bedrock (corestone 06PR35) for saprolite samples (a) and rindlet samples (b).

Figure 7: Variation of Zr concentration (in ppm) and Zr/Hf concentration ratios along the outcrop profile. The gray part represents the range of the corestone values.

Figure 8 : a) Depth variations of $^{87}Sr/^{86}Sr$ isotope ratios and of ε_{Nd} in the outcrop profile b) Depth variations of U and Th concentrations (in ppm) and of U/Th concentration ratio in the outcrop profile c) depth variation of the ^{238}U-^{234}U-^{230}Th-^{226}Ra disequilibria and of the ($^{230}Th/^{232}Th$) activity ratios within the profile. The plain line give the secular equilibrium value (activity ratios =1). Error bars are within the symbol size. Same symbols as Fig. 7.

Figure 9: Figure 9: Plot of εNd versus $^{87}Sr/^{86}Sr$ ratios for samples of the outcrop profile. (data source: this study; Pett-Ridge et al., 2009). The mixing curves are calculated between quartz diorite corestone and Saharan dust by changing [Sr] in the corestone in order to fit all the data from the regolith. (R = ([Sr]/[|Nd])corestone / ([Sr]/[|Nd])Saharan dust - R = 5.1 for the actual Sr concentration in the corestone (259 ppm), R= 1 for a Sr concentration of 50 ppm and R =0.1 for a Sr concentration of 3 ppm. Range of primary minerals is defined by the plagioclases and the biotites data, which have respectively the lowest ($^{87}Sr/^{86}Sr$~0.704) and the highest ($^{87}Sr/^{86}Sr \approx 0.72527$) ratios of the primary minerals of the Quartz diorite (Pett-Ridge et al., 2009).

Figure 10 : Measured ($^{234}U/^{238}U$) and ($^{230}Th/^{238}U$) activity ratios and ($^{230}Th/^{234}U$) and ($^{226}Ra/^{230}Th$) activity ratios for the lower saprolite (10a) and the 2004 rindlets (10b) (see text for definition). Dashed line indicates theoretical time evolution of activity ratios of the 06PR02 sample for saprolite (10a) and sample 3-8 for rindlets (10b) with parameters from Table 3 using the model described in the text (in configurations assuming a constant weathering rate for all the profile). Ages reported on the graph are the ages of the different samples relative to the sample 06PR02 (3-8 respectively), taken as the initial condition. The histogram gives the occurrence of the different production rates obtained on around 1000 retained runs of the simulation.

Appendix : A1-Solving the system of Eqs. (1)-(5)

We describe here the construction of the bound constrained optimization algorithm used to perform the calculation of the leaching rate constants: k_{238}, k_{234}, k_{230}, k_{226} and k_{232} , the input flux constants : f_{238}, f_{234}, f_{230}, f_{226} and f_{232} for each nuclide and the migration rates of the weathering front p. The model used is based on that presented by Dequincey et al., 2002 and Dosseto et al., 2008, modified by adding a mobility for ^{230}Th, ^{226}Ra and ^{232}Th. Solutions of the ordinary differential equation Eqs.(1)-(5) system are given in section A2. They were determined using Laplace transformations and the symbolic computer algebra system: Maxima 5.18.1.

For the lower saprolite and the rindlet zone used for weathering rate determination, measured (^{234}U/^{238}U), (^{230}Th/^{238}U), (^{226}Ra/^{230}Th), (^{238}U/^{232}Th) and (^{230}Th/^{232}Th) ratios in each sample are used to constrain the parameters of the model. Two different solving configurations are envisaged: the first one, without using ^{232}Th mobility, and hence, only (^{234}U/^{238}U), (^{230}Th/^{238}U) and (^{226}Ra/^{230}Th) ratios are modelled; the second one includes ^{232}Th mobility and (^{234}U/^{238}U), (^{230}Th/^{238}U), (^{226}Ra/^{230}Th), (^{238}U/^{232}Th) and (^{230}Th/^{232}Th) activity ratios are modelled. For the weathering rate P, two cases have been studied: one case is based on the implicit assumption of isovolumetric weathering where the regolith production rate P is considered to be constant through each profile. The other does not assumed an isovolumetric weathering; thus P can vary for each sample in the saprolite and rindlet zone (one P for each sample). Instead of the measured bedrock samples, the deepest sample from each zone was used to represent initials conditions.

The objective function is built by starting from a least square formulation using as input values measured radionuclide ratios with simple bounds on the variables $\mathbf{x}$ = (p; k_{238}; k_{234}; k_{230}; k_{226}; k_{232}; f_{238}; f_{234}; f_{230}; f_{226}; f_{232}). The aim of constraint optimization was to find a solution (parameters) that minimizes the sum of the square of the difference between observed and modelled values. For the first iterate, $\mathbf{x_0}$ is randomly computed within lower and upper bound. The algorithm uses a large-scale bound-constrained optimization solver: L-BFGS-B (Byrd et al., 1995 ; Zhu et al., 1997; Morales and Nocedal, 2011). It is a limited-memory quasi-Newton code (Broyden-Fletcher-Goldfarb-Shanno

1090 approximation of the Hessian matrix) for bound-constrained optimization, i.e. for problems where the
1091 only constraints are of the form $\boldsymbol{x_l \leq x \leq x_u}$. The vectors $\mathbf{x_l}$ and $\boldsymbol{x_u}$ are the vector of *lower* and *upper*
1092 *bounds* on the variables, respectively, and we allow either of them to have components -∞ or+∞. The
1093 gradients of the objective function related to each variables are numerically computed using a high
1094 precision numerical differentiation scheme (sixth order extrapolation rule).
1095 The model calculation was performed 1000 times to obtain parameter solutions for different random
1096 values for $\mathbf{x_0}$. The model calculates output parameters such that they fit the observed activity ratios
1097 with approximately less than 1% error. In all of our numerical studies, the number of model equation
1098 is equal to or greater than the number of unknown parameters: the system is over-determined.
1099

A2: Analytical solutions of the ordinary differential equations Eqs.(1)-(5)

(N.B.: The activity of each nuclide is determined by multiplying the solution by the decay constant of the nuclide)

$$U(t)=\frac{f_{238}\,{}^{238}U_0}{\alpha_{238}}+e^{-\lambda_{238}t}\left({}^{238}U_0-\frac{f_{238}\,{}^{238}U_0}{\alpha_{238}}\right)$$

$$U(t)=\frac{1}{\alpha_{234}}\left(f_{234}\,{}^{234}U_0+\lambda_{238}\frac{f_{238}\,{}^{238}U_0}{\alpha_{238}}\right)+e^{-\alpha_{238}t}\left({}^{238}U_0-\frac{f_{238}\,{}^{238}U_0}{\alpha_{238}}\right)\frac{\lambda_{238}}{\alpha_{234}-\alpha_{238}}+e^{-\alpha_{234}t}\left({}^{234}U_0-\frac{f_{234}\,{}^{234}U_0}{\alpha_{234}}+\left({}^{238}U_0-\frac{f_{238}\,{}^{238}U_0}{\alpha_{234}}\right)\frac{\lambda_{238}}{\alpha_{238}-\alpha_{234}}\right)$$

$$Th(t)=\frac{1}{\alpha_{230}}\left(f_{230}\,{}^{230}Th_0+\frac{\lambda_{234}}{\alpha_{234}}\left(f_{234}\,{}^{234}U_0+\lambda_{238}\frac{f_{238}\,{}^{238}U_0}{\alpha_{238}}\right)\right)+e^{-\alpha_{238}t}\left({}^{238}U_0-\frac{f_{238}\,{}^{238}U_0}{\alpha_{238}}\right)\frac{\lambda_{238}\lambda_{234}}{(\alpha_{234}-\alpha_{238})(\alpha_{230}-\alpha_{238})}+e^{-\alpha_{234}t}\left({}^{234}U_0-\frac{f_{234}\,{}^{234}U_0}{\alpha_{234}}+\left({}^{238}U_0-\frac{f_{238}\,{}^{238}U_0}{\alpha_{234}}\right)\frac{\lambda_{238}}{\alpha_{238}-\alpha_{234}}\right)\frac{\lambda_{234}}{\alpha_{230}-\alpha_{234}}+e^{-\alpha_{230}t}\left({}^{230}Th_0-\frac{f_{230}\,{}^{230}Th_0}{\alpha_{230}}+\frac{\lambda_{234}}{\alpha_{234}-\alpha_{230}}\left({}^{234}U_0-\frac{f_{234}\,{}^{234}U_0}{\alpha_{230}}+\left({}^{238}U_0-\frac{f_{238}\,{}^{238}U_0}{\alpha_{230}}\right)\frac{\lambda_{238}}{\alpha_{238}-\alpha_{230}}\right)\right)$$

$$Ra(t)=\frac{1}{\alpha_{226}}\left(f_{226}{}^{226}Ra_0+\frac{\lambda_{230}}{\alpha_{230}}\left(f_{230}{}^{230}Th_0+\frac{\lambda_{234}}{\alpha_{234}}\left(f_{234}{}^{234}U_0+\lambda_{238}\frac{f_{238}{}^{238}U_0}{\alpha_{238}}\right)\right)\right)$$
$$+e^{-\alpha_{238}t}\left({}^{238}U_0-\frac{f_{238}{}^{238}U_0}{\alpha_{238}}\right)\frac{\lambda_{238}\lambda_{234}\lambda_{230}}{(\alpha_{234}-\alpha_{238})(\alpha_{230}-\alpha_{238})(\alpha_{226}-\alpha_{238})}$$
$$+e^{-\alpha_{234}t}\left({}^{234}U_0-\frac{f_{234}{}^{234}U_0}{\alpha_{234}}+\left({}^{238}U_0-\frac{f_{238}{}^{238}U_0}{\alpha_{234}}\right)\frac{\lambda_{238}}{\alpha_{238}-\alpha_{234}}\right)\frac{\lambda_{234}\lambda_{230}}{(\alpha_{230}-\alpha_{234})(\alpha_{226}-\alpha_{234})}$$
$$+e^{-\alpha_{230}t}\left({}^{230}Th_0-\frac{f_{230}{}^{230}Th_0}{\alpha_{230}}+\frac{\lambda_{234}}{\alpha_{234}-\alpha_{230}}\left({}^{234}U_0-\frac{f_{234}{}^{234}U_0}{\alpha_{230}}+\left({}^{238}U_0-\frac{f_{238}{}^{238}U_0}{\alpha_{230}}\right)\frac{\lambda_{238}}{\alpha_{238}-\alpha_{230}}\right)\right)\frac{\lambda_{230}}{(\alpha_{226}-\alpha_{230})(}$$
$$+e^{-\alpha_{226}t}\left({}^{226}Ra_0-\frac{f_{226}{}^{226}Ra_0}{\alpha_{226}}+\frac{\lambda_{230}}{\alpha_{230}-\alpha_{226}}\left({}^{230}Th_0-\frac{f_{230}{}^{230}Th_0}{\alpha_{226}}+\frac{\lambda_{234}}{\alpha_{234}-\alpha_{226}}\left({}^{234}U_0-\frac{f_{234}{}^{234}U_0}{\alpha_{226}}+\left({}^{238}U_0-\frac{f_{238}\right.\right.\right.\right.$$
$$Th(t)=\frac{f_{232}{}^{232}Th_0}{\alpha_{232}}+e^{-\lambda_{232}t}\left({}^{232}Th_0-\frac{f_{232}{}^{232}Th_0}{\alpha_{232}}\right)$$

1108

1109 Here, we define

$$\alpha_{238}=\lambda_{238}+k_{238}$$
$$\alpha_{234}=\lambda_{234}+k_{234}$$
$$\alpha_{230}=\lambda_{230}+k_{230}$$
$$\alpha_{226}=\lambda_{226}+k_{226}$$
$$\alpha_{232}=\lambda_{232}+k_{232}$$

1117 and $^{238}U_0$, $^{234}U_0$, $^{230}Th_0$, $^{226}Ra_0$ and $^{232}Th_0$ are the initial number of atoms of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra and
1118 ^{232}Th respectively in the starting material.

Electronic annexes

EA1: Additional information concerning the 2006-rindlets

During the curse of the study, it was seen that the 2006 rindlet samples, collected for this study, were not suitable for the determination of a weathering propagation rate. For these reasons they have not been used in this study; A few additional information concerning these rindlets are given below.

The 2006 rindlets look from a mineralogical point of view like the gray rindlet reported in Turner et al. (2003). These authors indeed noticed the presence of two kinds of rindlets in the Rio Icacos watershed: (1) milky white and iron oxide stained rindlets, with characteristics very similar to that of the corestone and (2) uniformly thick gray rindlets with thinner ferric iron-stained inter-rindlet boundary zones. The origin of the latter has not really been discussed, and the study of the corestone weathering processes was essentially performed on the white/stained rindlets, because of their petrological similarities with the corestone mineralogy and texture (e.g., Turner e al., 2003; Buss et al., 2008).

The REE result and the Sr and Nd isotopic ratios obtained in our study show that the REE pattern of the 2006 rindlets and the Sr and Nd isotopic composition are very similar to those of the corestone and the 2004 rindlets. All together these data confirm the common magmatic origin of all these samples. However, the 2006 rindlets with their low and unusual Zr/Hf ratios and Ca and Mg enrichment correspond to locally appearing and specific magmatic differentiation and/or mixing patterns in the corestone. Therefore, the normalization to the average composition of the corestone, as made for the 2004 rindlets, might yield wrong element mobility estimations for the 2006 rindlets. Such normalisation can, however, still be used for estimating the relative mobility of chemical elements within the rindlets, if it is assumed that all of the rindlets originate from a same initial material; the data show, however, that there is no simple chemical evolution from the base to the top of the rindlet zone, except in the outermost 3-5 rindlets where a decrease of K, Na and Ca from the inner rindlets to the outer ones is observed. Instead, the deeper part could be subdivided into an inner portion, eventually marked by a slight decrease of K, Na and Ca, and an outer part, richer in Na Ca and Mg. The interpretation of this variation in terms of changing weathering intensity

is difficult. They rather reflect initial mineralogical variations between these different rindlets.

The variations of the U-Th concentrations and ^{238}U-^{234}U-^{230}Th-^{226}Ra isotope systematics in the 2006 rindlets are very different and more complex than these of the 2003-2004 remnant rindlets, except maybe for the ($^{234}U/^{238}U$) which is >1. Their U concentrations are also higher than those of the corestone samples, but their Th concentrations are much lower. This might be related to the peculiar mineralogical characteristics of these rindlets. The variations of the ($^{238}U/^{232}Th$) and Th activity ratios show very similar evolutions with first an important increase from the corestone to the middle of the rindlet zone, and then with a decrease to values observed in the saprolite basement (Fig.9). The origin of such variations is not really understood at this stage; however as variations of Th isotopic ratios and of U/Th ratios seem to be different in the two zones of the 2006 rindlets (defined on the basis of major element characteristics), they could be linked to primary mineral variations within this specifical magmatic system. A Detailed mineralogical analysis of these rindlets similar to that performed for the other type of rindlets (Buss et al., 2008) would be required to confirm such a conclusion. This was clearly outside the scope of this study. At this time, and without a better understanding of the origin of the U-Th-variation within these rindlets it seems hazardous to use them for estimating the progression rate of weathering front within the rindlet zone.